# ABNORMAL FORMATION OF PYRAZOLO[1,5-a]PYRIDINES VIA THE DESULFURIZATION OF PYRIDO[1,2-b]-4,1,2-THIADIAZINE INTERMEDIATES

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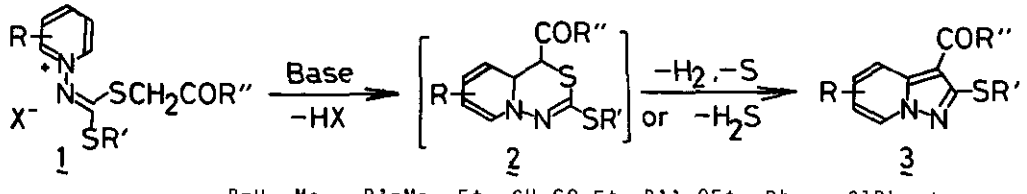
In the course of our investigation for preparing some nitrogen-bridged heterocycles such as indolizines and pyrazolo[1,5-a]pyridines, we have recently described some convenient synthetic methods for these heterocycles. In particular, compounds, thus obtained, were appropriately functionalized, and their versatility as precursors for further condensed heterocycles were also indicated.[1-4] This report provides the results and discussion on a novel and unusual synthetic method for functionalized pyrazolo[1,5-a]pyridine derivatives by the alkaline treatment of pyridinium salts possessing an isocyanate dithioacetal group at the 1-position.

In order to introduce a substituent involving an active methylene group onto the 2-position of pyrazol[1,5-a]pyridine, when the reactions of pyridinium salts 1 with various reagents in the presence of alkali were carried out, the initially expected products could not be obtained at all. However, the unexpected intramolecular cyclization products, 3-acyl-2-alkylthiopyrazolo[1,5-a]pyridines 3, were formed directly in considerable yields. The generality and the wide applicability of this reaction were proved immediately by the uses of various pyridinium salts 1. Mechanistically, it is clear that pyrido[1,2-b]-4,1,2-thiadiazine intermediates 2 must be involved in this reaction, and our attempts to detect such intriguing molecules will be also dicussed.




1 2 3

R=H, Me R'=Me, Et, $CH_2CO_2Et$ R''=OEt, Ph, p-ClPh etc.

References

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